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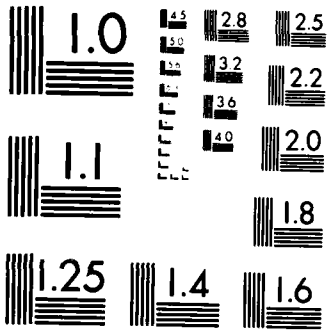

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RESEARCH IN PHASE TRANSFER CATALYSIS

by Janos H. Fendler, PhD

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US Army Armament, Munitions & Chemical Command
Aberdeen Proving Ground, Maryland 21010-5423

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Mechanisms for the hydrolysis of paratoluenesulfonyl fluoride (pTSF) in the aqueous sodium hydroxide cyclohexane two-phase system have been elucidated for different phase transfer catalysts. The mechanism for the hydrolysis is composite; it involves both interfacial and phase transfer catalysis. Experimental conditions determine the mechanism(s) which prevails.

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PREFACE

This research was authorized by Contract No. DAAK11-79-C-0111, titled "Research on Phase Transfer Catalysis," with the Chemical Systems Laboratory, ARRADCOM,* sponsored through the US Army Research Office. The work was started in December 1979 and completed in December 1980.

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RESEARCH IN PHASE TRANSFER CATALYSIS

1. INTRODUCTION

Advantages of microheterogeneous systems for the detoxification of arylsulfonyl halides became evident recently to the Chemical Systems Laboratory*. Microheterogeneous systems are capable of solubilizing and localizing such materials and providing media for their catalytic degradation. Research had shown that aqueous nucleophilic and functional micelles, microemulsions, and polyelectrolytes were powerful media for the destruction of selected arylsulfonyl halides. An alternative approach is provided by phase transfer catalytic systems.

Phase transfer catalysis is an extremely useful and versatile synthesis technique.[1-6] Its relative simplicity, speed, and economy have rendered this method invaluable for large scale industrial processes. Indeed, new syntheses and gross improvements of existing ones have mushroomed. To date, more than 2000 papers have been published on phase transfer catalysis. Only a handful of these are concerned, however, with mechanistic aspects.[7-13]

The phase transfer mechanism, proposed initially by Starks for nucleophilic substitution,[7] involves the transfer of the nucleophile, Y^-, from water to the organic phase where substitution on RX occurs. The leaving group, X^-, is subsequently transported back to water. Transport of the anions is accomplished by an organic soluble phase transfer agent, typically a quaternary ammonium or phosphonium halide, Q^+Y^-:

$$\begin{array}{ccccccc} RX & + & Q^+Y^- & \longrightarrow & RY & + & Q^+X^- \\ & & & \text{organic phase} & & & \\ \hline & & & \text{water} & & & \\ Na^+Y^- & + & Q^+X^- & \longrightarrow & Na^+X^- & + & Q^+Y^- \end{array} \qquad (1)$$

There are two basic tenets of the proposed mechanism. Firstly, the reaction is assumed to take place in the organic phase, rather than in water or at the interface of two immiscible solvents. Secondly, formation of both aqueous and reversed micelles is precluded. The observed kinetic behavior of nucleophilic substitions under phase transfer conditions constituted evidence for mechanism 1. Specifically, rate constants

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were found to (a) increase linearly with increasing catalyst concentrations, (b) increase with the ability of the catalyst to extract the anion into the organic phase, and (c) remain invariant of the stirring rate (beyond 300 rpm). Kinetic schemes have recently been derived for phase transfer catalyses characterized by mechanisms analogous to that given in equation 1.[5,10] These derivations implicitly assume that the transfer of the reagent from the aqueous to the organic phase is fast compared to the substitution. Reactions other than nucleophilic substitutions may well be governed by rate-limiting transfer of the reagent across the boundary separating the phases. Indeed, acceptance of mechanism 1 for all reactions occurring in two-phase immiscible systems is not warranted. Conceivably, reaction sites may involve the polar-apolar solvent interface.

2. OBJECTIVES

The objective of this research has been to examine the feasibility of phase transfer catalysis as a viable hydrolytic method. Rates and mechanisms for the destruction of paratoluenesulfonyl fluoride have been determined under phase transfer catalytic conditions.

3. EXPERIMENTAL

3.1 Preparation of Tetra-n-butyl-phosphonium Hydroxide (Bu_4POH)

Tetra-n-butyl-phosphonium bromide (Bu_4PBr), Aldrich, was recrystallized from ethyl acetate. Ten milliliters of 10 M aqueous Bu_4PBr was shaken 30 minutes with 3.0 gm of AG_2O and centrifuged. A bromide ion selective electrode was used to determine the extent of the reaction. No bromide ion could be detected after completion of the exchange.

3.2 Synthesis of [1-^{14}C] Bu_4PBr

1-^{14}C-labelled Bu_4PBr was made by refluxing 0.010 moles of tri-n-butyl-phosphine with 0.10 moles of [1-^{14}C] n-butyl bromide (specific activity = 3.87 mCi/mmol) in 2 ml of absolute ethanol in a sealed ampoule at 85°C for 160 hours. The reaction was stopped by cooling the ampoule with liquid nitrogen. After distilling off the solvent, a saturated solution of Bu_4PBr in 10 ml of hot ethyl acetate was poured into the ampoule. The crystallized product was washed with cool ethyl acetate and dried under vacuum overnight. The resulting product had a specific activity of 0.81 mCi/mole (yield = 10%).

3.3 Distribution Coefficients of Quaternary Ions.

Base concentrations in the organic phase were determined as described by Herriott and Picker.[8] Distribution coefficients of Bu_4P^+ ion and H_2O between water and cyclohexane were determined using 1-^{14}C Bu_4POH or bromide (.817 mCi/mol) and ^3H H_2O (0.074 mCi/Mol). Radioactivities were counted on a Beckman SL100 scintillation counter using a ^{137}CS external standard to correct for quenching.

3.4 Kinetics of Hydrolysis of Paratoluenesulfonyl Floride (pTSF).

Kinetics runs were carried out in a 100-ml two-necked flask fitted with a stirring motor. The stirring speed was determined with a stroboscopic tachometer at least three times during the kinetic run. The reaction vessel was immersed in a constant temperature bath. The temperature inside the flask was maintained at 25.0° ± 0.5°C. Usually 15 ml of cyclohexane phase was stirred with 50 ml of a 4 M NaOH water solution of the catalyst. The reaction was stopped by pouring out an aliquot of cyclohexane phase over spectranalyzed grade cyclohexane to the proper dilution. Concentrations of pTSF were determined spectrophotometrically at 267 nm using a Cary 118C spectrophotometer.

4. RESULTS AND DISCUSSION

4.1 Hydrolysis of p-Toluenesulfonyl Fluoride.

Rate constants for the hydrolysis of p-toluenesulfonyl fluoride have been redetermined in the phase transfer system using tetrabutylphosphonium bromide (Bu_4PBr) as catalyst. Particular emphasis has been placed on determining the concentration of the hydroxide ion in the organic phase and examining the effects of an added electrolyte on the hydrolysis rate. The results are contained in Table 1. It is seen that sodium chloride does not appreciably alter the rate of hydrolysis in the absence of catalyst. This result obviates the need for investigating the influence of electrolytes on partitioning p-toluenesulfonyl fluoride between water and cyclohexane. Rate constants for the hydrolysis of p-toluenesulfonyl fluoride in the phase transfer system in the presence of increasing amounts of Bu_4PBr are given in Tables 2 and 3. Rate constants in all cases had been followed to 99.5% completion of the reaction. The agreement is good between rate constants determined in the cyclohexane and in the aqueous phases, and the correlation coefficients are excellent. The catalytic efficiency of the transfer agent is impressive. Rate enhancement as a function of added catalyst is linear (see Figure A-1), but, as a function of OH^- concentration in the cyclohexane phase, the rate increase is shown to be exponential (see Figure A-2).

Table 1. Hydrolysis of p-Toluensulfonyl Fluoride*
in H_2O-Cyclohexane in the Absence of Phase
Transfer Catalyst at 25.0°C

[NaOH], M in H_2O	$10^5[OH^-]$, M in cyclohexane	10^3k_ψ, sec^{-1} in cyclohexane	r	10^3k_ψ, sec^{-1} in H_2O	r
1.0	4.0	3.1	.9996	2.66	.9996
2.0	6.0	3.6	.9989	3.1	.99[illegible]
3.01	6.0	1.71	.9998	1.6	.9987
3.82	8.0	1.63	.9968	1.3	.998[illegible]
2.0 + 2.0M NaCl		2.15	.9985		

*Determined spectrophotometrically. All rates were followed to 99.95% completions.

Table 2. Hydrolysis of p-Toluenesulfonyl Fluoride*
in H_2O-Cyclohexane in the Presence of Phase
Transfer Catalyst at 25.0°C

10^3 $[Bu_4PBr]$, M in H_2O	10^4 $[OH^-]$, M in cyclohexane	10^3k_ψ, sec^{-1} in cyclohexane	r	10^3k_ψ, sec^{-1} in H_2O	r
0.0	0.80	1.63	.9968	1.30	.9980
6.5		2.90	.9965	2.90	.998-1.00
7.5		2.82	.9991	2.67	.9995
10.0	5.0	4.50	.9980	3.67	.9938
12.0		3.10	.9960	3.00	.9982
20.0	14.0	4.20	.9960	2.90	.9913
30.0	21.5	8.07	.9117	2.58	.9904
40.0	24.5	10.80	.9740	6.50	.9927
50.0	17.0	17.50	.9804	19.80	.9180
100.0	32.0	41.20	.9980		

*Determined spectrophotometrically. All rates were followed to 99.95% completion.

Table 3. Hydrolysis of p-Toluenesulfonyl Fluoride*
in the Presence of Different Types of Catalysts

Catalyst	$10^3 k_\psi$, sec^{-1} in cyclohexane	10^4 $[OH^{-1}]$ in cyclohexane
10 mM $(Bu_4P)_2SO_4$	1.7	4.8
10 mM Bu_4PBr	2.9	5.0
Uncatalyzed	1.6	0.8
10 mM $Bu_3PBuOHCl$	2.3	1.4
10 mM Bu_4POH	3.44	34.3
50 mM Bu_4POH	36.75	39.0
50 mM Bu_4PBr	27.0	17.5

*Determined spectrophotometrically. All rates were followed to 99.95% completion.

4.2 Synthesis of Tris-butyl-(4-hydroxybutyl)phosphonium Chloride.

A phase transfer agent capable of forming an internal ion pair with hydroxide ion may be a more efficient catalyst than Bu_4P^+Br. With this in mind, tris-butyl-(4-hydroxybutyl)phosphonium chloride was synthesized. The reaction was started by addition of an ethanolic solution of 4-chlorobutanol to tributylphosphine. After four days, the reaction was shown to be complete by means of a chloride ion selective electrode using a potentiometer. Stirring was continued for an additional day to ensure that there was no saturation effect of the product, phosphonium chloride (see Figure A-3). The solvents and reagents were then evaporated under vacuum (1 mm Hg at 170°C, the boiling point of Bu_3P). The remaining solid was dissolved in water and then extracted with ethyl ether. Long plates crystallized from the ether extract after one week. The water extract did not crystallize, but both products showed the same NMR and IR spectrum. NMR spectrum: $-CH_3$, 9H, 3.3 ppm; $-CH_2-$, 26 H, 1.6 ppm; -OH, 1H, 1.0 ppm. The observed ratio of -OH to $-CH_3$, plus $-CH_2-$ = 1:35.22.) IR spectrum: S 3.4 μ, 3.5 μ; W 4.05 μ; W 6.1 μ; M 7.1, 7.25, 7.45, 7.7 μ; S 8.2, 8.7 μ M 9.2, 9.5, 10.0, 10.3, 11 μ; S 13.2 μ. The alcohol signal was identified by derivitization with acetic anhydride or trifluoracetic acid; OH bands at 3400-3300 cm^{-1} disappeared.

Rate constants for the hydrolysis of p-toluenesulfonyl fluoride were determined by titrating the cyclohexane phase as a function of time, as described by Herriott and Picker.[8] $Bu_3(HOBu)PCT$ appeared to be a much better catalyst than Bu_4PBr.

5. MECHANISTIC INVESTIGATIONS

Figure A-4 shows the effect of changes in concentration of tetrabutylphosphonium hydroxide (Bu_4POH) and changes in stirring speed upon the pseudo-first-order hydrolysis rate constants for paratoluenesulfonyl fluoride (pTSF) in the two component aqueous 4 M NaOH system. The rate is seen to increase with increasing stirring speeds at all catalyst concentrations. At the lowest catalyst concentration (30 mM) there is a hint of leveling off. Clearly rates do not level off at concentrations of 40 mM and 50mM Bu_4POH. Figure A-5 compares the catalytic efficiencies of Bu_4POH and tetrabutylphosphonium bromide, Bu_4PBr, as a function of stirring speed. Although the extractability of Br^- is several hundredfold greater than OH^-, appearance of a third oily phase in the presence of Bu_4PBr is at least partially responsible for the poorer performance of this catalyst. The solid thick line in Figure A-5 shows the effect of stirring speed on the rates for a nucleophilic substitution under true phase transfer conditions.

The mechanism for the hydrolysis of pTSF in the present aqueous 4 M NaOH-cyclohexane two-phase system is clearly different from that described by pure phase transfer catalysis. Coexistence of interfacial and phase transfer catalysis is more probable although a phase transfer mechanism prevails to a greater extent for Bu_4PBr than for Bu_4POH. Under our experimental conditions, most of the Bu_4POH catalyzed hydrolysis of pTSF appeared to occur at the water-cyclohexane interface.

5.1 Effect of Catalyst Concentration.

Concentrations of Bu_4PBr and Bu_4POH in the organic phase were measured by a bromide selective electrode and by titration, respectively. The observed rate for the hydrolysis of pTSF increase exponentially with increasing catalyst concentrations at all stirring speeds as indicated in Figures A-6 and A-7. At very low stirring speeds, the kinetics followed zero-order rate laws which became pseudo-first order at stirring speeds greater than 350 rpm. Similarly, in the presence of catalyst concentrations above at 0.03 M, the observed kinetics are pseudo-first order at any stirring speed. We interpret this behavior to be a change of mechanism from rate determining transport of the reagent to rate determining hydrolysis.

5.2 Distribution of Water, Catalysts, and Products Between the Aqueous and Organic Phases.

The catalyst and water concentrations in the organic phase as a function of separation time following centrifugation are shown in Figure A-8. Interestingly, the catalyst concentration in the organic phase is independent of the nature of the counter ion. Importantly, the distribution of both the catalyst and water decrease exponentially to a low level as a function of phase separation time. Concentrations of water and catalyst are, therefore, extremely high during the reaction at the interface. Paratoluenesulfonic acid, the product of the hydrolysis of the fluoride, is soluble in cyclohexane. Unlike Starks and Liotta, we did not find the hydrolysis to be inhibited by added paratoluenesulfonic acid. This is not compatible with the notion that phosphonium salts act only as phase transfer agents.

5.3 Effect of Changes in the Volume Ratios of Water to Cyclohexane.

Changes of the ratios of water to cyclohexane dramatically affect the rate of hydrolysis (Figure A-9). Increasing the volume ratio of water to cyclohexane increases the rate twelvefold. Increasing the volumes of both phases also

increases the hydrolysis rate. These observations can be rationalized in terms of creating larger interfacial areas for the hydrolysis by increasing volumes, increasing stirring speed, and increasing ratios of water.

5.4 Partitioning of the p-Toluenesulfonyl Fluoride, pTSF.

Using the standard U-tube with cyclohexane in the two arms, we studied the transport of pTSF from one side of the U-tube across an aqueous solution containing NaOH and Bu_4POH.

The kinetics of transport appeared to follow the zero-order rate law. This result substantiates our postulate that, in the presence of catalysts and at appropriate stirring speed, transport of the reagents across the interface is fast compared to the rate of hydrolysis.

6. CONCLUSION

Studies under this contract have demonstrated the utility of phase transfer catalysis for the hydrolysis of paratoluenesulfonyl fluoride. Substantial enhancements of the hydrolysis rates have been elicited. The mechanism for the hydrolysis appears to involve both interfacial and phase transfer catalyses. Experimental conditions determined the prevailing mechanism.

Based on these studies, further investigations in order to optimize phase transfer catalysis, as well as for critical comparison of this method with others available, are recommended.

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APPENDIX

FIGURES

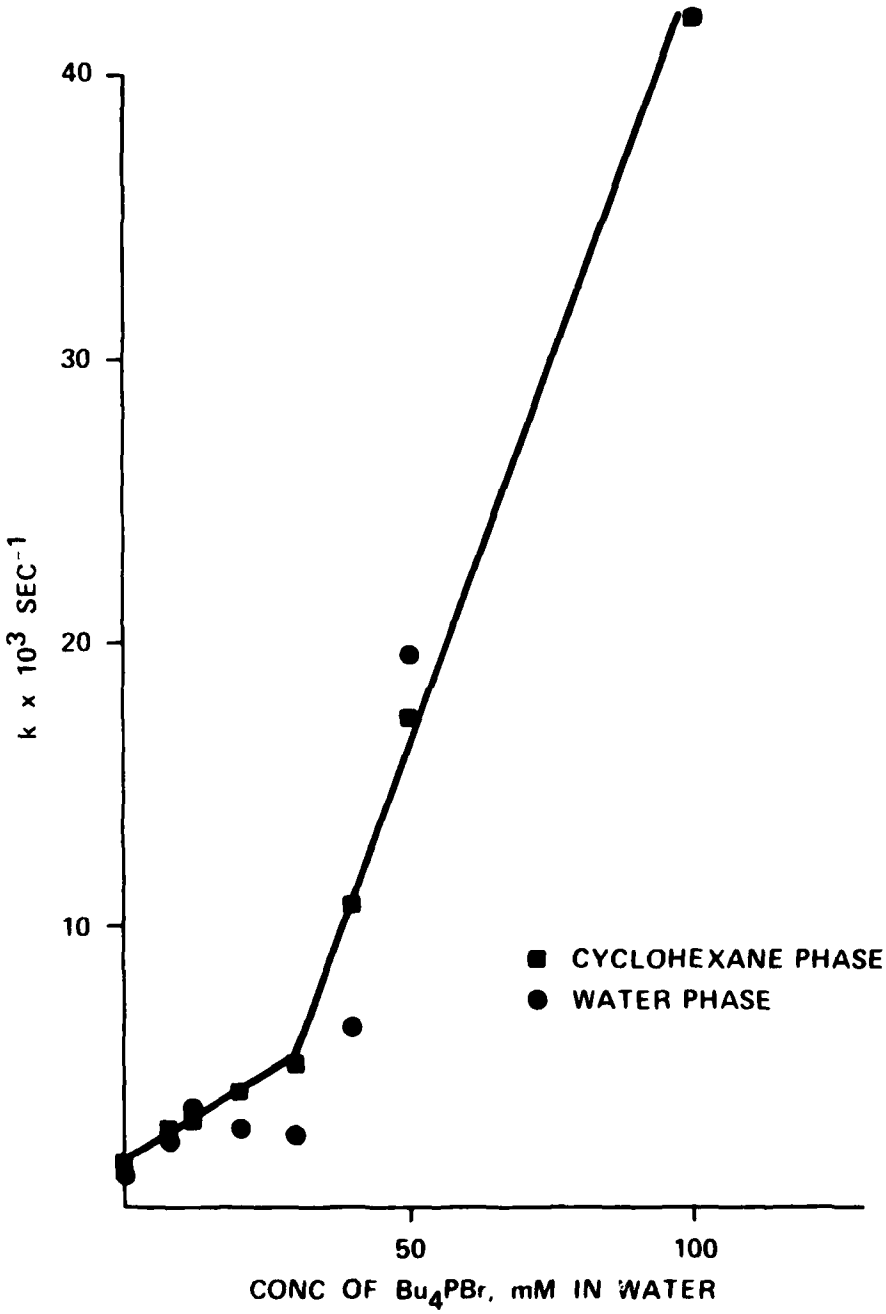

Figure A-1. Effect of Catalyst on Hydrolysis of PTSF

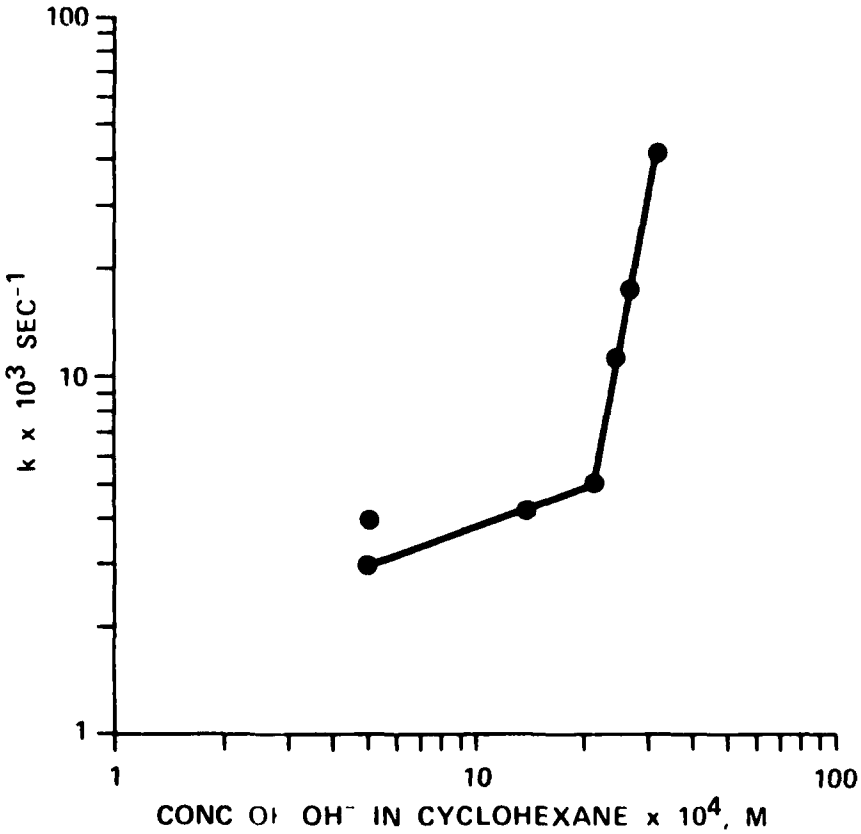

Figure A-2. Effect of Concentration of Hydroxyl ion in Cyclohexane Phase on Hydrolysis of PTSF

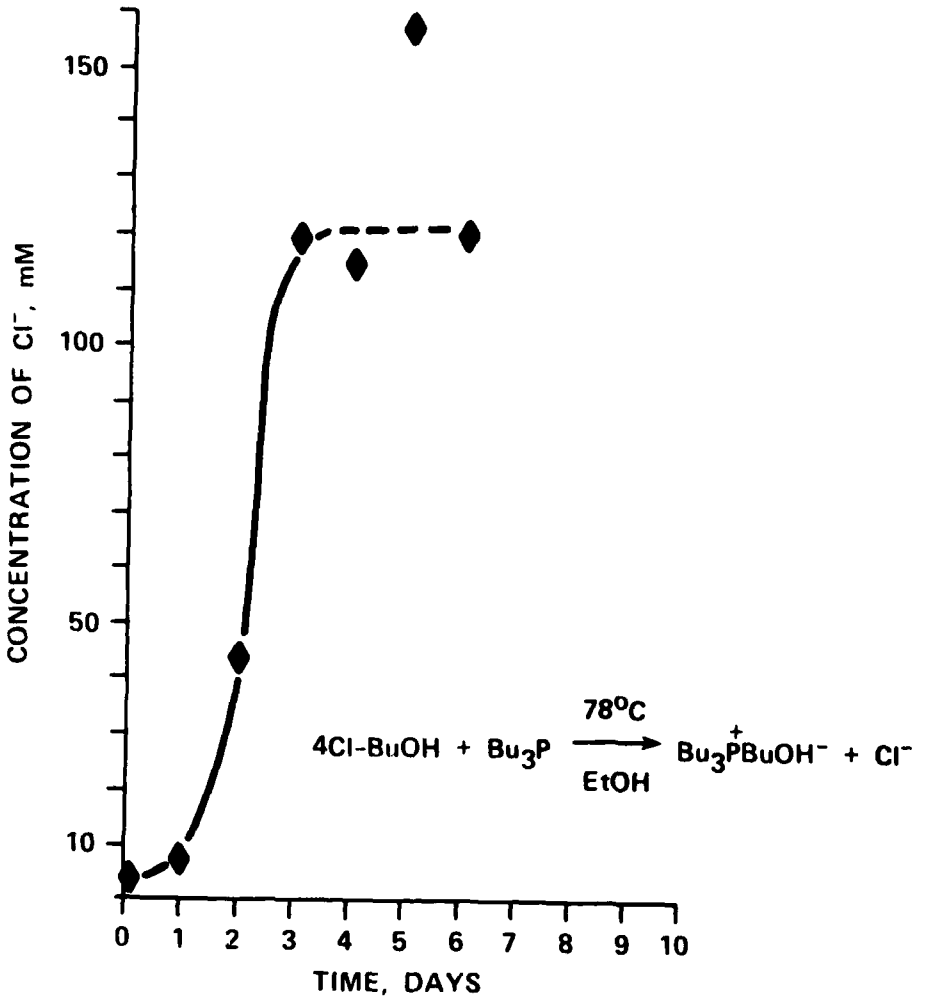

Figure A-3. Formation of Tributyl 4-hydroxybutylphosphonium Chloride

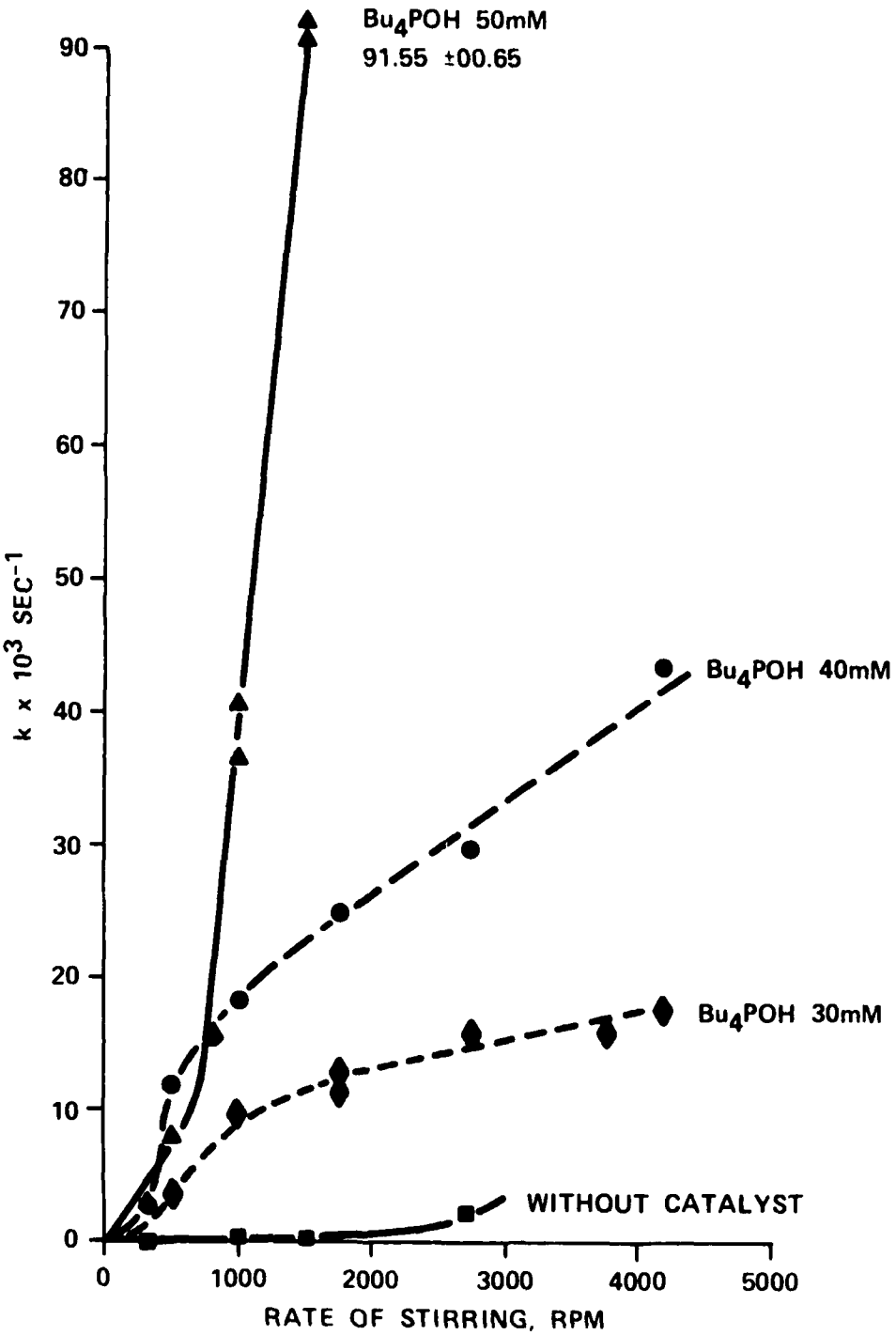

Figure A-4. Effect of Rate of Stirring on Hydrolysis of PTSF Using $Bu_4P^+OH^-$

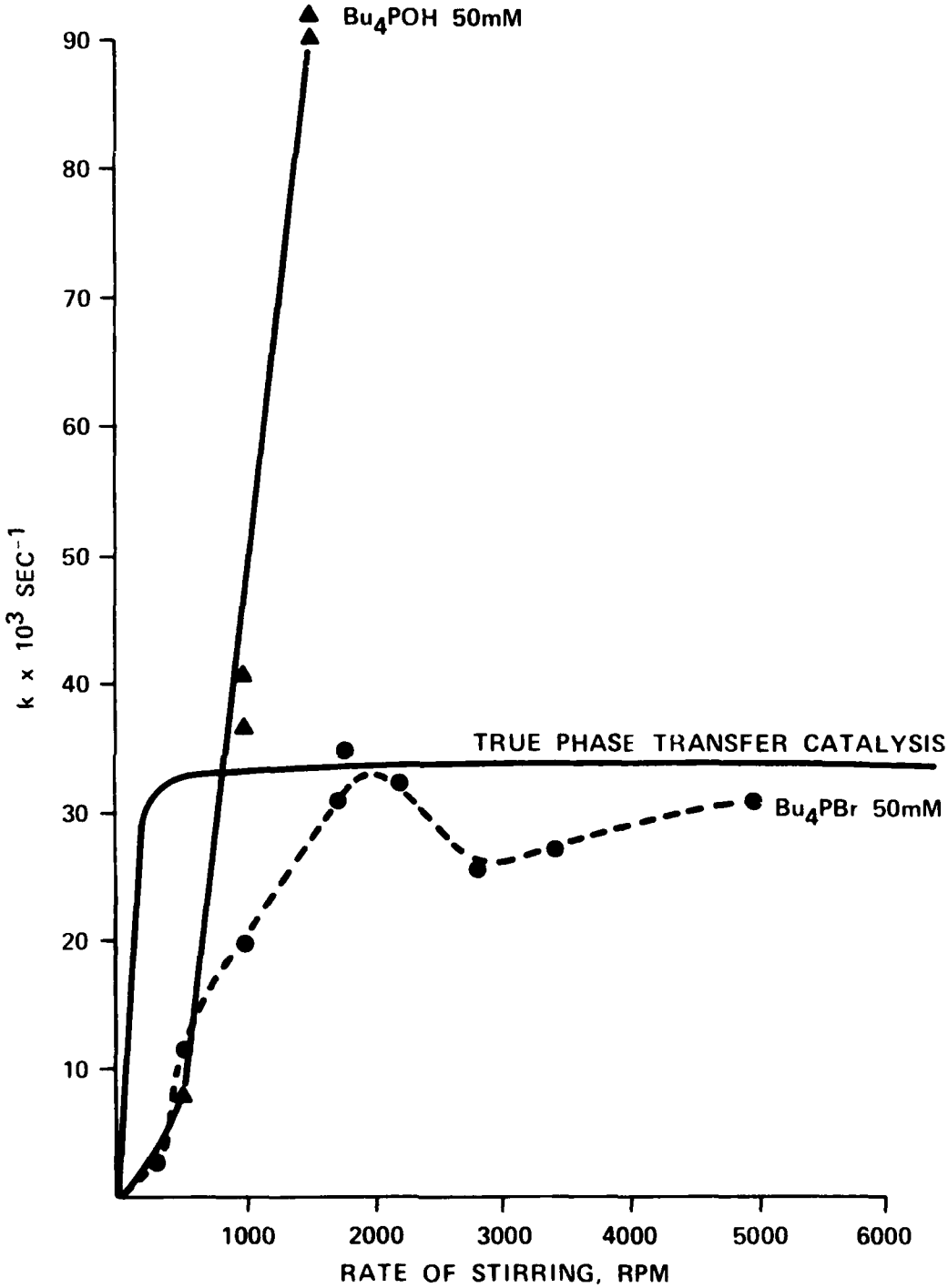

Figure A-5. Effect of Rate of Stirring on Hydrolysis of PTSF, Using Bu_4POH and Bu_4PBr

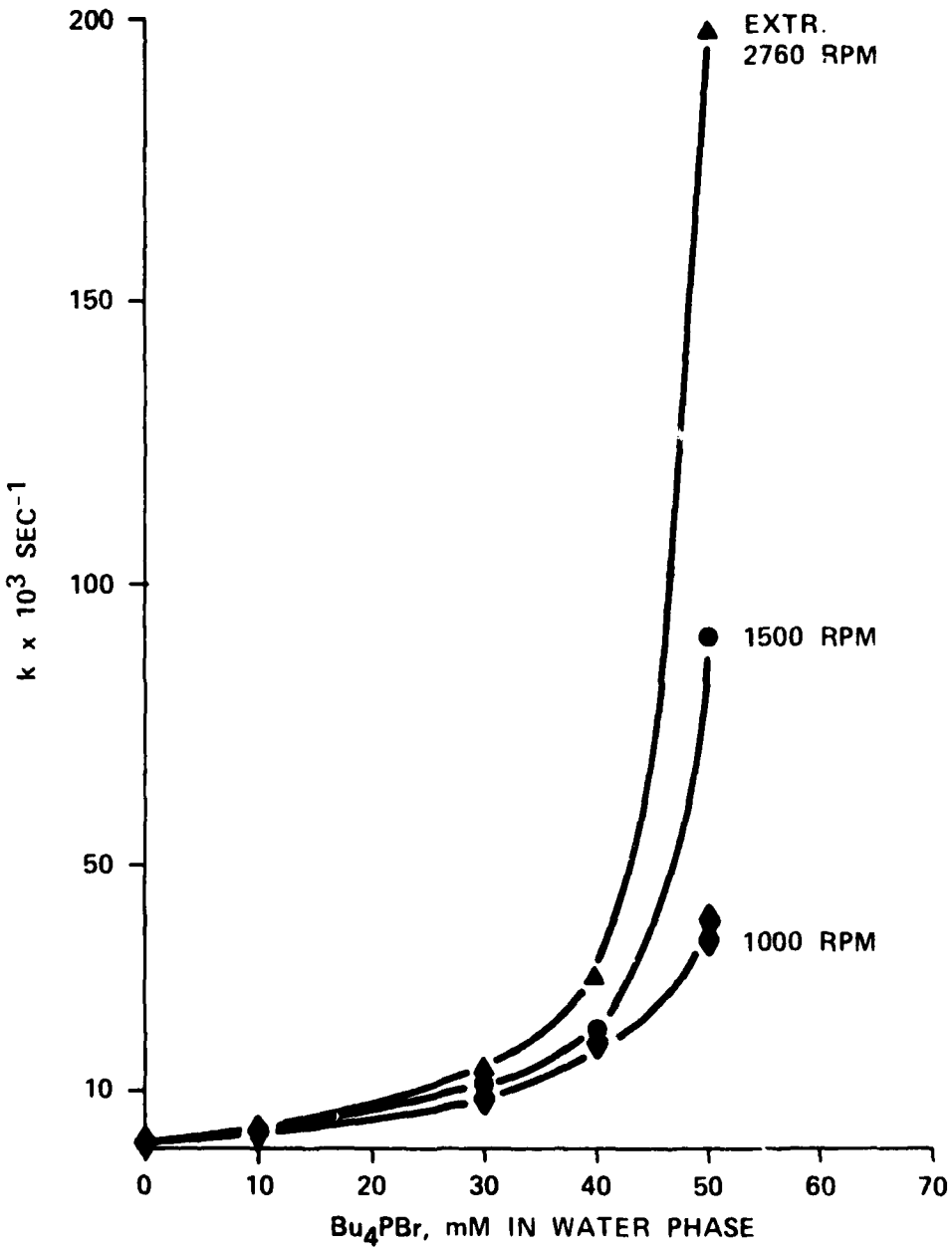

Figure A-6. Effect of Cencentration of Catalyst in Water Phase and Rate of Stirring Upon the Hydrolysis of PTSF

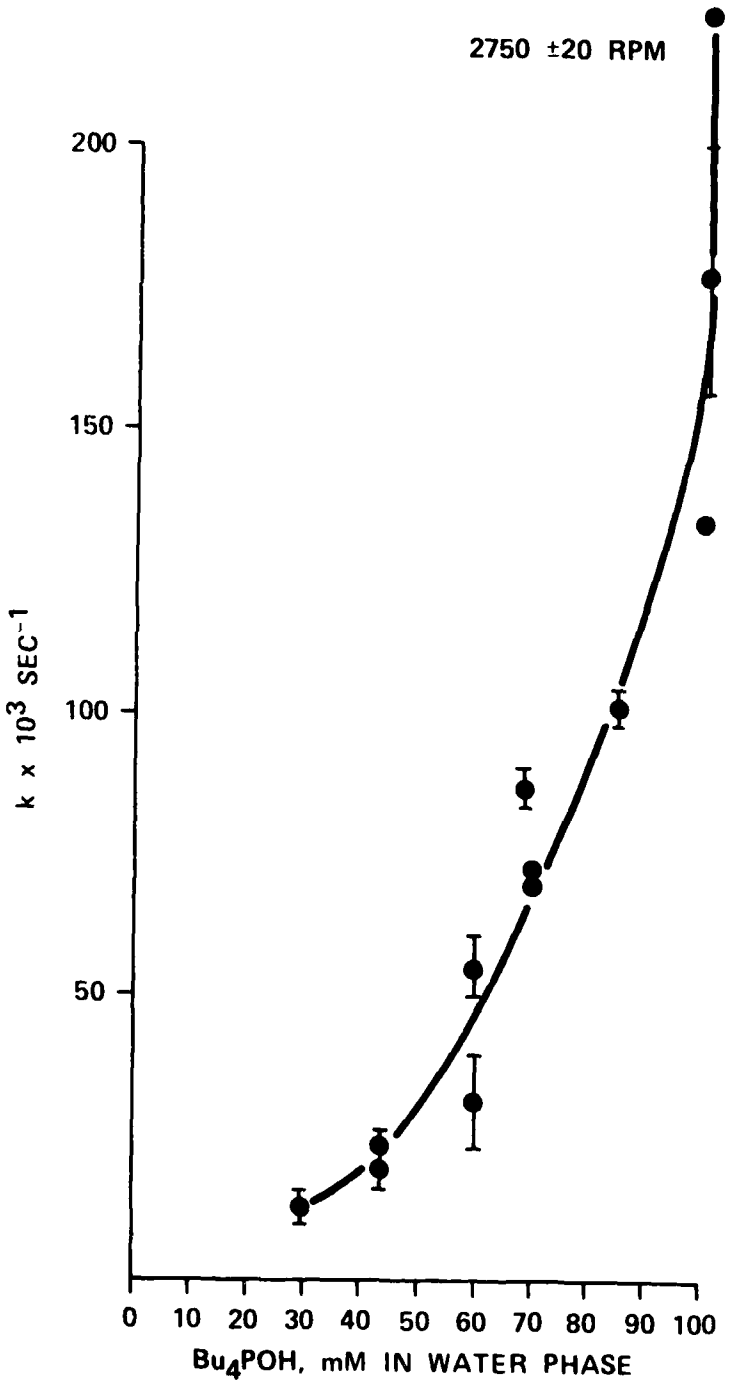

Figure A-7. Effect of Concentration of Catalyst in Water Phase on Hydrolysis of PTSF

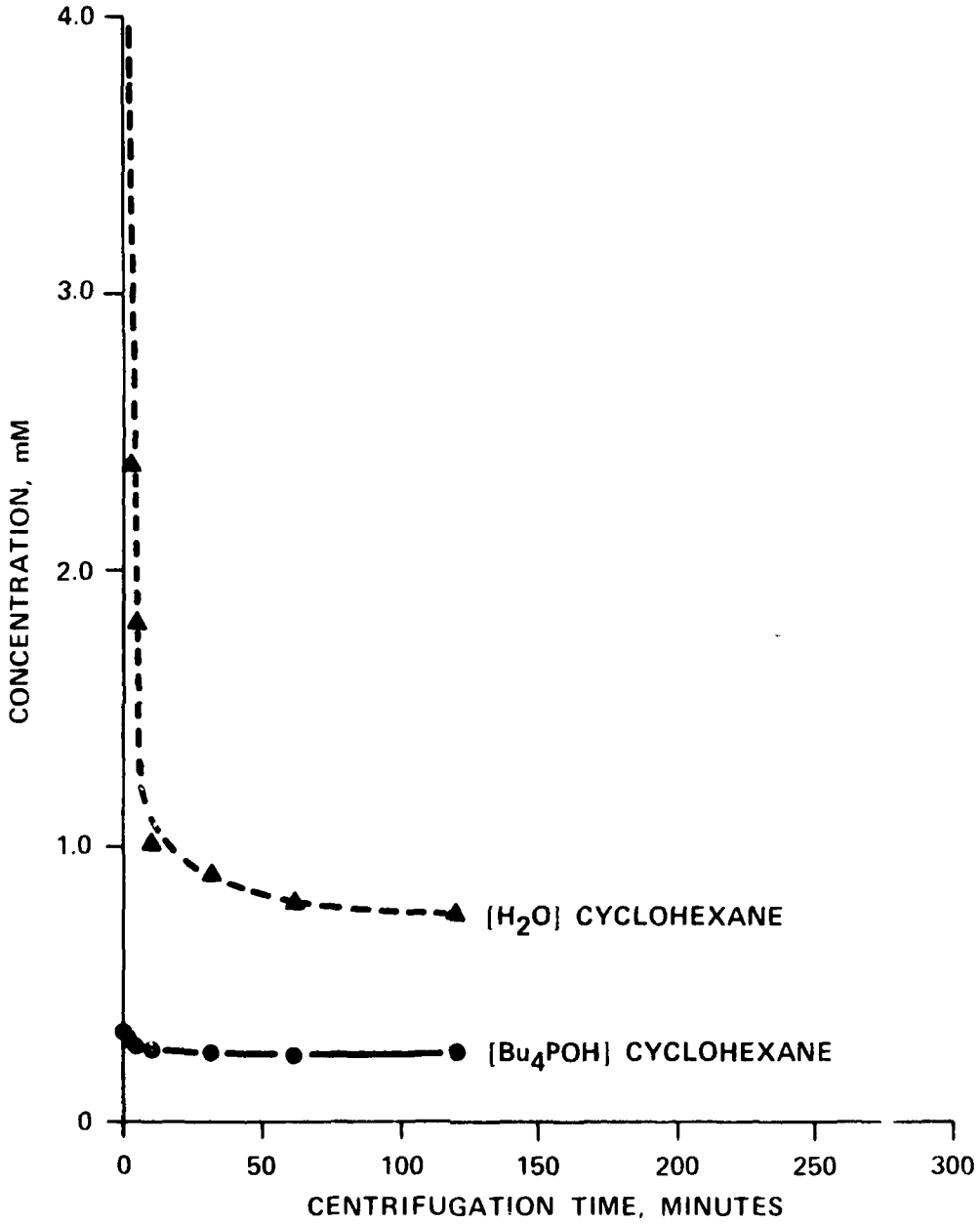

Figure A-8. Effect of Separation Time Upon Concentration of Catalyst in Cyclohexane Phase

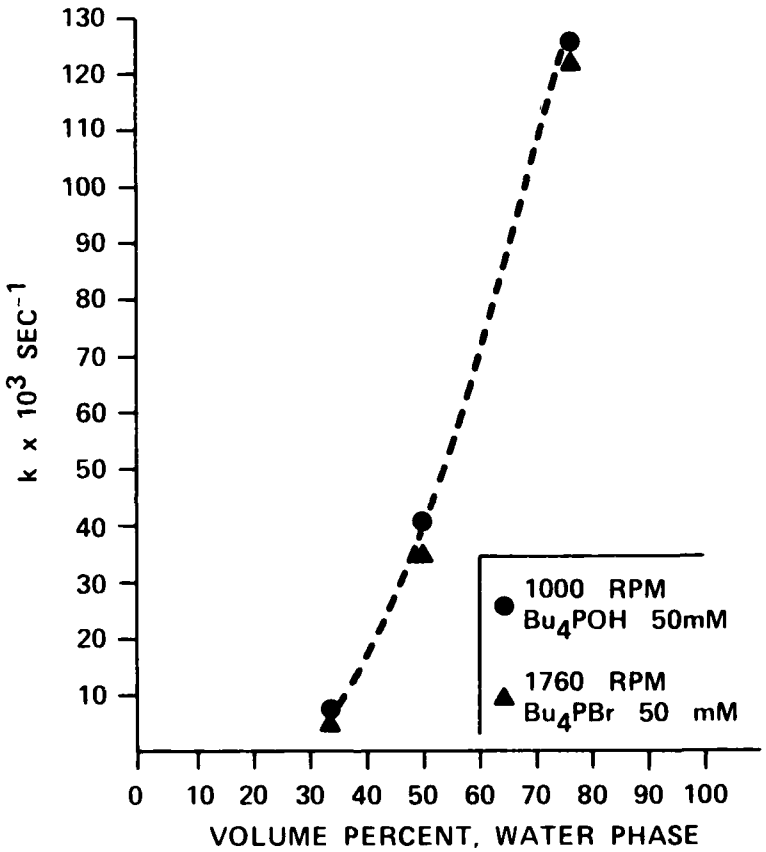

Figure A-9. Effect of Ratio of Water to Cyclohexane Phase on Hydrolysis of PTSF

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